

# Buffer pH Methods: Ongoing Iowa Laboratory and Field Studies <sup>1</sup>

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## Introduction

Soil acidity can affect plant growth directly and indirectly by affecting the plant-availability of nutrients, levels of phytotoxic elements, and microbial activity. Soils may become acidic in the long term as a result of several natural processes. In the short term, however, soil acidity develops mainly due to application of N fertilizers or manure, primarily those having high concentrations of ammonium or urea because nitrification releases hydrogen (H) ions. Soil pH decreases as the acidity increases because pH expresses acidity as the negative logarithm of concentration (activity) of H<sup>+</sup> ions. Changing soil pH requires changing the balance of acids and bases in both the soil water and on the cation exchange capacity of the soil. Soils have a capacity to release additional H<sup>+</sup> ions (often referred to as reserve acidity) which depends largely on the concentrations of clay and organic matter. Therefore, soil pH is used to determine whether or not to lime a soil but not to indicate the quantity of acid that should be neutralized. Direct titration of soil acidity seldom is used in the U.S., and a buffer test often is used to determine the lime requirement. Buffer solutions have a large capacity to resist a change in pH. The amount of lime needed to increase pH to a desirable level can be estimated by mixing a buffer of known pH with soil and measuring the resulting pH decrease. Low buffer pH values indicate high reserve acidity and lime requirement. Laboratory tests estimate acidity released over a short period of time, however, and at the field often additional acidity is released over time.

In Iowa, as in most Midwestern states, the Shoemaker-McLean-Pratt (SMP) buffer adjusted to pH 7.5 is used to estimate the lime requirement of soils (Shoemaker et al., 1961; Watson and Brown, 1998). Buffers used in other states are original or modified versions of Woodruff (Woodruff, 1948; Watson and Brown, 1998), Adams-Evans (Adams and Evans, 1962), and Mehlich (Mehlich, 1976) methods. These tests were developed before federal laws regulated disposal of hazardous waste due to ignitability, corrosivity, reactivity, or toxicity. Chemicals in this category are p-nitrophenol and potassium chromate in the SMP buffer and barium chloride in the Mehlich buffer. Work has been done to develop alternative methods for determining lime needs without using hazardous chemicals. For example, some labs are using direct titration with calcium hydroxide (Liu et al., 2005). Hoskins (2005) and Wolf and Beegle (2005) modified the Mehlich buffer by replacing barium chloride with calcium chloride. A disadvantage of the modified Mehlich is a short shelf life of only a few weeks. Sikora (2006) replaced potassium chromate and p-nitrophenol in the original SMP method by 2-(N-morpholino) ethanesulfonic acid monohydrate (MES) and imidazole. He compared the two methods using many soil samples from Kentucky and from other regions using samples of the North American Proficiency Testing (NAPT) program. He concluded that the modified buffer results in the same buffer pH value as the SMP buffer and had good stability over 150 days. Godsey et al. (2007) evaluated SMP and the modified Mehlich buffers in Kansas soils based on laboratory soil incubations and field limestone application. They reported that buffer pH values were significantly lower for the Mehlich buffer, and that with the local calibration this method would predict lime requirement better than the SMP buffer.

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This presentation summarizes comparisons of SMP, modified SMP by (i.e, Sikora), and modified Mehlich methods on the basis of laboratory analysis and field limestone application trials. The primary objective of the field trials is to establish a critical pH level for corn and soybean and summarized results are presented. Analyses of soil samples collected before applying lime and also after applying lime and harvesting one crop were used to compare the buffer methods. Evaluations will continue for a second crop year to study yield and responses to lime as well as buffer methods prediction of lime requirement over a longer period of time.

### **Summary of Procedures**

Ten field trials were established in Iowa farmers' fields, five in 2007 and five in 2008. The project uses dense soil sampling and precision agriculture technologies based on replicated treatments applied to long strips. Custom applicators' equipment, calibrated yield monitors, GPS, and GIS were used. Treatments are no lime or a uniform lime rate of 3 ton of effective calcium carbonate equivalent (ECCE)/acre. The CCE application rate was the same within a field but ranged from 3.7 to 5.9 ton CCE/acre across fields due to differences in limestone fineness. With the only exception of one no-till field, soil management included chisel-plow and disk tillage before soybean and only disking before corn. The limestone was incorporated with the tillage. Table 1 summarizes the most relevant site information. Soil samples were collected from a 6-inch depth before applying lime using a dense grid sampling approach, by which one 12-core composite sample was collected from cells ranging from 0.3 to 0.5 acres depending on the field. Soil pH and SMP buffer pH were measured by the method currently used in the Iowa, which is the recommended for the North Central Region (Watson and Brown, 1998). The Sikora buffer pH was measured as suggested by Sikora (2006) and the modified Mehlich buffer pH was measured as suggested by Hoskins (2005). The soil:water:buffer ratio was 1:1:2 for the SMP method and 1:1:1 for Sikora and Mehlich methods. Buffer solution final pH was 7.5 for SMP, 7.7 for Sikora, and 6.6 for Mehlich. Post-harvest soil samples were collected from limed soil sampling cells after one corn or soybean crop and were analyzed for pH to calculate the change from initial pH due to lime application. The pH and buffer pH results from initial soil samples (before applying lime) as expected showed large within-field variation for both measurements. Therefore, we use the soil-test data from each soil sampling cell for comparing buffer pH methods within and across fields. In addition, we compared buffer pH values for the SMP and Sikora methods based on 1,252 Iowa farmers' soil samples submitted to the Iowa State University (ISU) Soil and Plant Analysis Laboratory. These samples were collected from a much wider range of soil series and conditions than for the ten field trials. The soil series were indicated by the farmers, however, and could not be confirmed with certainty.

### **Summary of Findings** **Analysis of farmers' soil samples**

Data in Figs. 1 and 2 show the relationship between SMP and Sikora buffer pH values for the farmers' soil samples and the frequency distribution of differences between the methods. The buffer pH values for the two methods correlated very well. The coefficient of determination was high ( $r^2 = 0.85$ ), on average the difference between the two methods was only 0.01 pH units, and 76% of the differences were within  $\pm 0.01$  pH units. At this time we are correlating

the data for different soil series and for groups of samples according to soil organic matter. However, the high correlation and the fact that the vast majority of the differences between the two methods were small suggest that the good relationship will hold for different Iowa soils included in this set of samples. Such a similarity between these two methods was shown before for several Kentucky soils and several NAPT soil samples (Sikora, 2005) and for Wisconsin soils (Peters and Laboski, 2007).

### Results from the field trials

Very large soil pH and yield response variability along the long strips of the strip trials confirmed the value of dense soil sampling, yield monitors, and GPS for field-scale on-farm research using strip trials. At this time yield responses for within-field areas with different initial soil pH have been summarized only for the first five trials (harvested in Fall 2007). Results from this first year across the five fields indicated that corn and soybean responded to limestone application when soil pH was  $< 6.5$  (Fig. 3). The magnitude of the average yield response was small, but previous research has demonstrated a larger long-term impact of lime application. Study of soil-test results for samples collected from the ten field trials indicated that the within-field variability of initial soil pH and organic matter along the long strips was very large in all fields (Table 1). Study of only average soil pH and buffer pH values for each field would have resulted in a much lower range of values and probably misleading conclusions.

The buffer pH values for the Sikora and Mehlich methods from the ten field trials correlated well with the currently used SMP method within and across fields (Fig. 4). The coefficients of determination across all samples were high for all relationships ( $r^2 = 0.84$  to  $0.95$ ), being lowest between SMP and Mehlich and highest between Sikora and Mehlich. This was an interesting result, because we expected that the highest correlation would be between the SMP and Sikora methods. Analyses of results by field or for each soil series included in the study (see the two most dominant soil series at each trial in Table 1) did not show important deviations from the general relationship (not shown). The data and statistical analysis of relationships for the SMP and Sikora methods indicated that means did not differ significantly and the slope of the regression line did not differ from a value of 1.0. This is the same result that was found for the Iowa farmers' samples (Fig. 1) and by research with soils of other regions (Sikora, 2005; Peters and Laboski, 2007). In spite of a good correlation the relationships for the Mehlich method showed that the buffer pH values were significantly lower than for the SMP and Sikora methods, which is a consequence of the type of buffer used. This difference also was shown for other soils of the Midwest (Godsay et al., 2007; Peters and Laboski, 2007), although the difference varied across states confirming a need for local calibrations to determine lime requirements.

Study of relationships between buffer pH values by the three methods and initial soil pH showed a significant relationship between buffer pH and soil pH for all methods ( $r^2 = 0.48$  to  $0.62$ ), although the slope of the regression lines was significantly different for 2007 and 2008. Contrary to expectations, we found a very poor and statistically non-significant relationship between buffer pH values and soil organic matter ( $r^2 = 0.05$  to  $0.16$ ). Adding organic matter as a second variable to the equation relating buffer pH and soil pH did not result in a statistically significant improvement for any buffer method. Moreover, the field pH change due to applying 3 ton ECCE/acre was decreased significantly with increasing initial pH ( $r^2 = 0.44$ ) but was very

poorly related to soil organic matter ( $r^2 = 0.14$ ). This result might be explained by large effects of soil texture variation (texture has not been measured yet) and relatively small variation of organic matter levels in these soils (Table 1).

The field methods used in this study did not allow for field calibrations of lime requirement equations for the buffer methods because only one limestone rate was applied in all fields. Also, the available post-lime pH data are only for the first year after lime application. Previous research has shown that agricultural limestone often continues raising soil pH two years after being applied. A field calibration is needed (and field plots with this objective are being established in 2009) especially for the Mehlich buffer and also to confirm equations for the SMP and Sikora methods. We used the first-year post-lime pH values to further study relationships between the buffer methods, however. Data in Fig. 5 show how the buffer pH values by the three methods was related to soil pH change in the field resulting from applying lime at 3 ton ECCE/acre by eliminating absolute buffer pH differences between the methods. To calculate the plotted values we first calculated the pH change due to lime application by subtracting the initial soil pH value from the post-harvest pH value of limed strips, and then expressed the pH change per unit of buffer pH measured by each method. As expected based on relationships between buffer pH values in Fig. 4, the correlation between the three buffer methods was very high and the slope of the lines for the three relationships did not deviate significantly from 1.0. These results confirm that other than for lower buffer pH values for the Mehlich method, the three buffer methods correlated similarly with the field pH change due to limestone application.

### **Preliminary Conclusions**

Results of comparisons based on laboratory analyses and first-year field pH change due to application of a single limestone rate indicated that SMP, Sikora, and Mehlich buffer methods would be similarly effective at estimating lime requirement of Iowa soils. Because the SMP and Sikora buffer pH values were essentially the same, current calibrations and recommendations for the SMP method can also be used for the Sikora method. An advantage of the Sikora buffer method is that it does not include hazardous chemicals. Use the Mehlich buffer to estimate lime requirements with confidence requires field calibrations that could not be conducted with the methods used. The study will continue by evaluating relationships for pH change after a second year and by conducting multiple-rate trials needed to field calibrate the buffer methods.

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Table 1. Summary of site characteristics for ten replicated strip field trials.

Site	Crop year	County	Dominant soil series		N <sup>†</sup>	pH (range)	OM <sup>‡</sup> (range)	Limestone application <sup>§</sup>
			First	Second				
1	2007	Jasper	Clarion	-	32	6.0 (5.6-7.3)	3.3 (2.2-4.4)	May 18 2007
2	2007	Story	Webster	Nicollet	40	6.0 (5.7-7.2)	4.4 (2.7-7.2)	May 25 2007
3	2007	Boone	Canisteo	Nicollet	36	5.2 (4.8-6.0)	3.8 (2.6-5.2)	Nov 14 2006
4	2007	Greene	Canisteo	Okoboji	32	6.5 (5.1-8.1)	5.2 (3.6-7.8)	Oct 28 2006
5	2007	Boone	Talcot	Dickman	40	5.0 (4.6-5.8)	3.3 (1.2-4.7)	Jan 27 2007
6	2008	Cedar	Dinsdale	Muscatine	36	5.5 (5.2-6.7)	3.4 (2.3-3.8)	May 12 2008
7	2008	O'Brien	Primghar	Galva	36	5.5 (5.2-6.0)	5.2 (4.5-5.7)	Nov 9 2007
8	2008	O'Brien	Galva	-	36	5.9 (5.2-6.7)	4.9 (4.5-6.0)	Nov 9 2007
9	2008	O'Brien	Marcus	Primghar	36	5.7 (5.5-6.1)	6.9 (5.3-9.2)	Apr 15 2008
10	2008	Union	Sharpsburg	Clarinda	19	5.6 (4.8-6.2)	4.0 (3.4-4.7)	Apr 28 2008

<sup>†</sup> N, number of samples (grid cells). <sup>‡</sup> OM, organic matter %. <sup>§</sup> The limestone was incorporated by chisel-plow/disk or disk tillage in Sites 1 through 9 but was not incorporated at Site 10 (a no-till field).

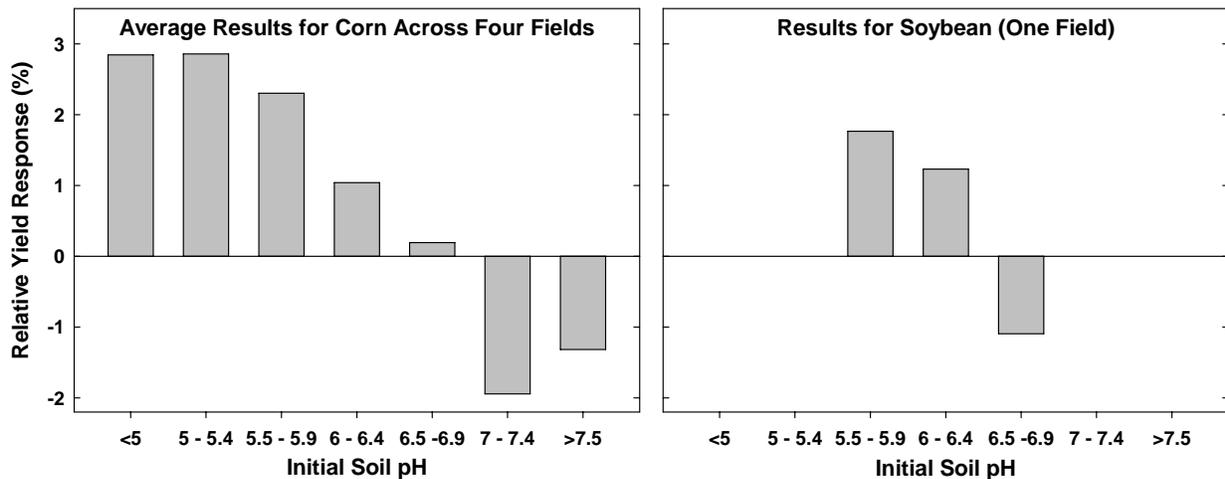


Fig. 1. Grain yield response of corn (4 fields) and soybean (one field) to 3 ton ECCE/acre for several soil pH ranges (2007).

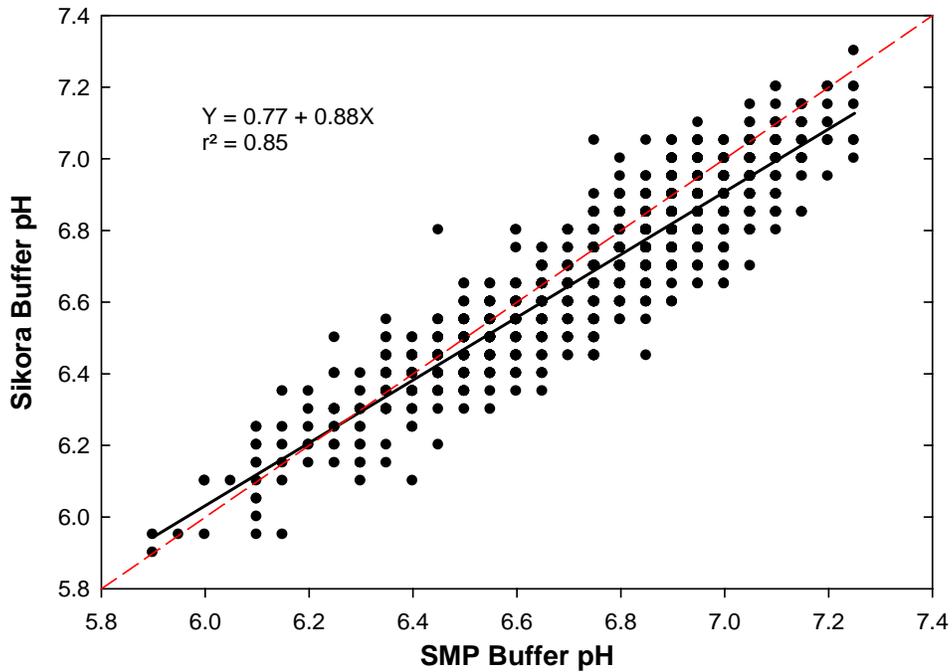


Fig. 2. Relationship between buffer pH by SMP and Sikora methods for 1,252 Iowa soil samples submitted by farmers to the Iowa State University Soil and Plant Analysis Laboratory.

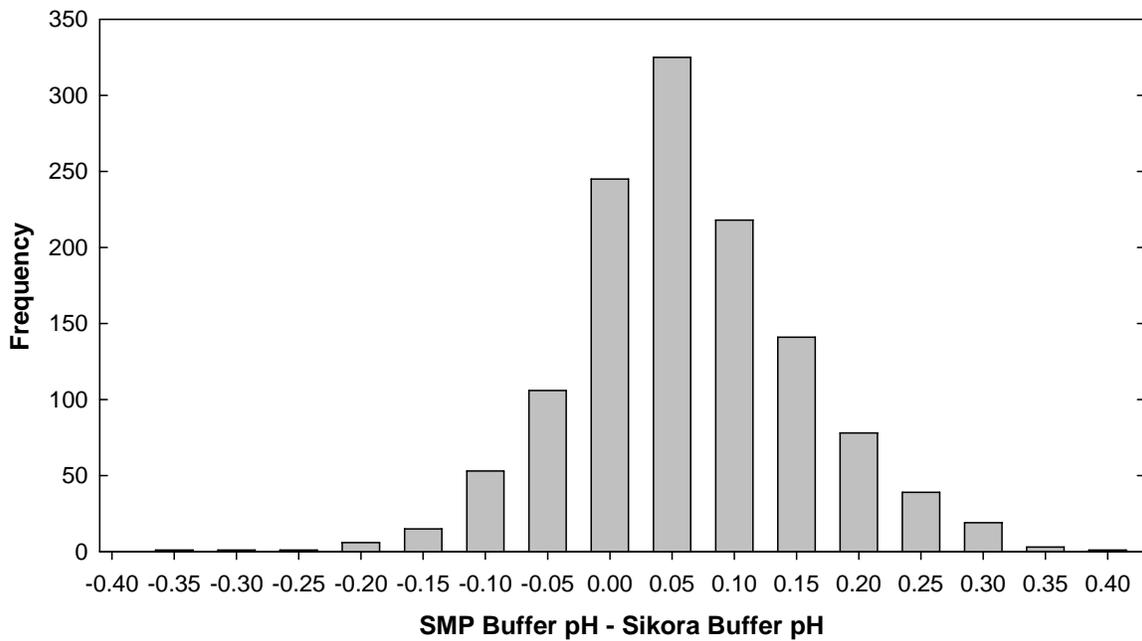


Fig. 3. Frequency distribution of differences between the SMP and Sikora buffer pH methods for 1,252 soil samples submitted by farmers to the Iowa State University Soil and Plant Analysis laboratory.

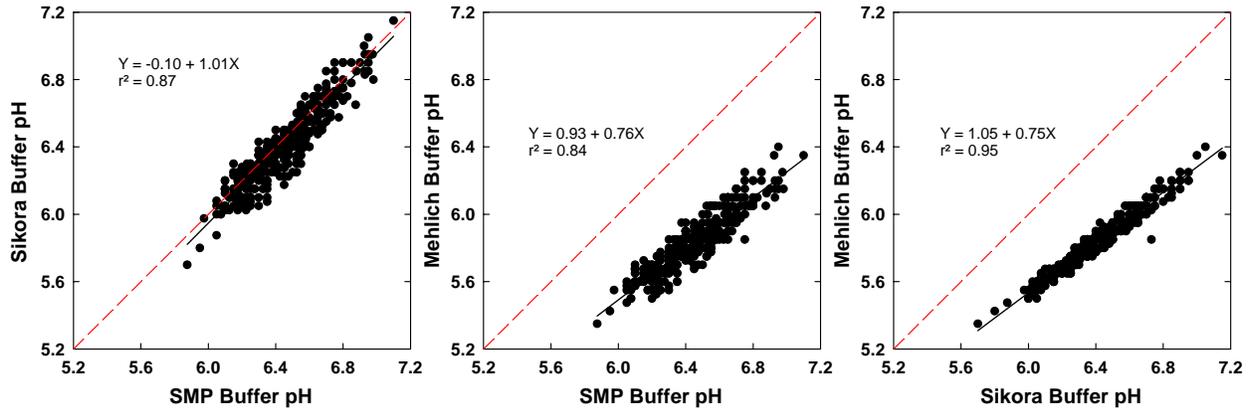


Fig. 4. Relationships between buffer pH values measured with SMP, Sikora, and Mehlich methods for soils samples collected from ten Iowa field trials before lime application.

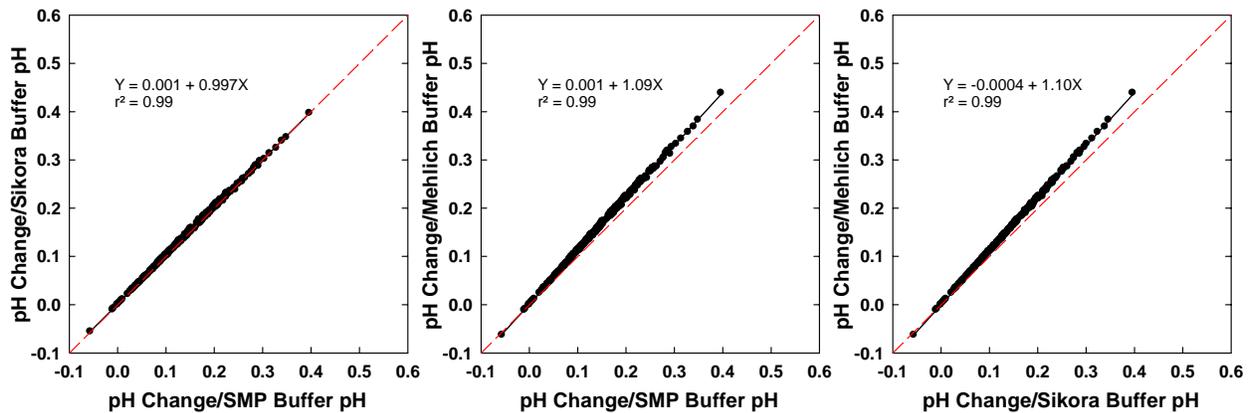


Fig. 5. Relationships between the soil pH change resulting from applying 3 ton ECCE/acre expressed as the change per unit of buffer pH measured by SMP, Sikora, and Mehlich buffer methods.